AEC-NASA TECH BRIEF

Electrolytic Separation of Crystals of Transition-Metal Oxides

The problem:

To develop a method of growing crystals of the transition-metal oxides, which have important uses in the microwave (radar) field, and applications as lasers and masers in communications. The growth of large crystals is difficult because the melting points of many of these mixtures are higher than the dissociation temperature of the oxides at atmospheric pressure. The chromite series of compounds, while usually quite stable, have extremely high melting points ($\geq 2000°C$); they present the problem of finding a container that is both inert and resistant to such temperatures.

The solution:

An extremely versatile flux system has been developed for growing large, well-formed, stoichiometric single crystals of mixed oxides of the transition-metal elements. Single crystals of $M^{++}Cr_2O_4$ and $M^{++}Fe_2O_4$ (where M^{++} is a transition or alkaline-earth ion) and the garnet $Y_3Fe_5O_{12}$ have been grown from the sodium tungstate-pyrotungstate flux system $(1-x)Na_2W_2O_7-xNa_2WO_4$, where $1 \geq x \geq O$. In addition, single crystals of the system $Co_{1+\delta}V_{2-\delta}O_4$ (where $1 \geq x \geq O$) have been prepared by electrolysis of $CoO-V_2O_5$ mixtures dissolved in a suitable sodium polytungstate flux.

The phase boundaries present in the $CoCr_2O_4-Na_2W_2O_7-Na_2WO_4$ system are determined, and generally discussed is a solution process for transition-metal oxides in a sodium pyrotungstate flux formulated on Lewis acid-base theory.
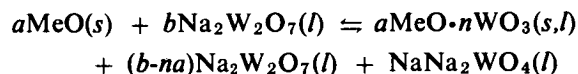
How it's done:

Fundamentally the polytungstate-flux system can be described in terms of Lewis acid-base theory. The basic oxides are dissolved by a strong Lewis acid

(WO_3) and then reprecipitated by a strong Lewis base (Na_2WO_4). This process of solution and reprecipitation can be expressed by the equilibrium equation $Na_2W_2O_7$ (l) $\leftrightharpoons$ Na_2WO_4 (l) + WO_3 (l).

Sodium pyrotungstate ($Na_2W_2O_7$) is a relatively stable compound at low temperatures, dissociating only slightly into the acid-base components. As the temperature increases, the equilibrium is shifted rapidly toward the right. Consequently, at higher temperatures, more acid is produced to dissolve the transition-metal oxides as complex tungstates, the process reversing as the temperature decreases.

Therefore the only requirements for solubility of a particular transition-metal oxide (or mixture of oxides) at a temperature T are that (1) a complex tungstate, of the transition-metal oxide, must exist at T that is at least partially soluble in the flux system; and (2) it must be possible to establish at T an equilibrium reaction by which the complex tungstate is formed through reaction of the metal oxide with a finite amount of sodium pyrotungstate.

The solubility requirements imply the existence of an equilibrium reaction at T of the type

$$aMeO(s) + bNa_2W_2O_7(l) \leftrightharpoons aMeO \cdot nWO_3(s,l)$$
$$+ (b-na)Na_2W_2O_7(l) + NaNa_2WO_4(l)$$

where $MeO \cdot nWO_3(s,l)$ is a partially soluble complex tungstate of a transition-metal oxide MeO. Thus, if a moles of a transition-metal oxide are added to the flux composition at T, there exists a value of $x(x_c)$ above which the only solid phase that may exist in equilibrium with the solution is the transition-metal oxide. The value of x_c is expected to increase as the relative basicity of the oxides increases and to be largest for alkali and alkaline-earth oxides.

If a flux composition is chosen for which $x = x_c + \Delta x$ at temperature T, the amount of solid oxide in equilibrium with the solution will decrease as the temperature is raised to $T + \Delta T$. This dissolved oxide may then be reprecipitated at any desired rate on subsequent cooling. Slow rates of cooling are desirable for growth of large single crystals.

Notes:

1. This information may interest the electronics and communications industries.
2. U.S. Patent No. 3 382 161 covers this innovation.
3. Inquiries concerning this innovation may be directed to:

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Patent status:

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